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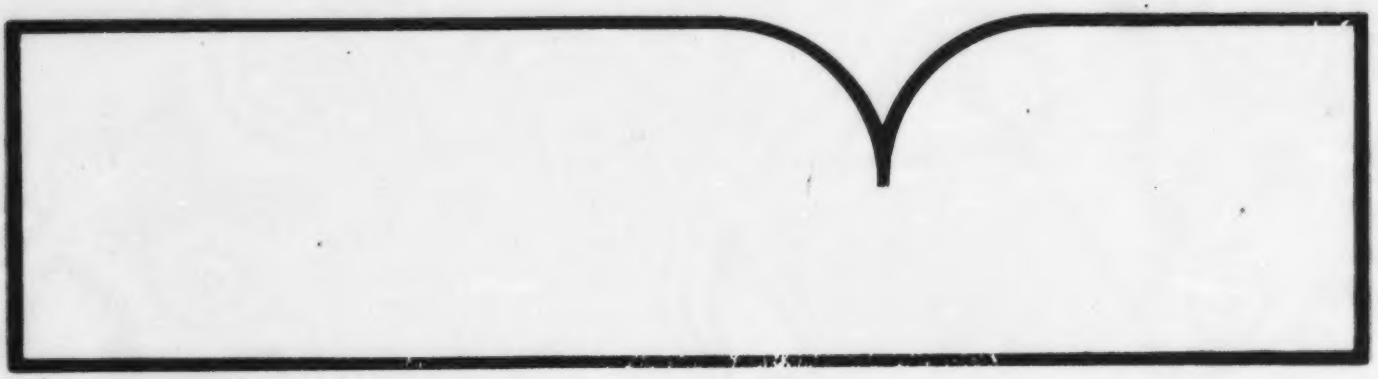
Dynamic Dilution System for Auditing Ambient Sulfur Dioxide Analyzers

Environmental Monitoring Systems Lab.
Research Triangle Park, NC

Aug 83



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16. ABSTRACT

This paper discusses the development, evaluation, and field performance of a device designed to provide accurate sulfur dioxide concentration standards suitable for auditing the accuracy of continuous, ambient SO_2 monitors. This compact, lightweight, device has been subjected to extensive testing and found to be a reliable and accurate SO_2 audit system. A discussion of the evaluation and acceptance testing as well as the results from two years of field audits is presented.

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DYNAMIC DILUTION SYSTEM FOR AUDITING AMBIENT SULFUR DIOXIDE ANALYZERS

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INTRODUCTION

Since 1980, EPA's Environmental Monitoring Systems Laboratory at Research Triangle Park, NC (EMSL-RTP) has been using a portable dilution system to audit the performance of continuous SO_2 monitors. This paper describes the testing involved in the development of this device and summarizes the results achieved since its introduction into the National Performance Audit Program.

The advance in SO_2 measurement technology from manual wet chemical methods to continuous monitors caused EMSL-RTP to initiate development of a system to be used in a nationwide audit of continuous SO_2 analyzers. In order to be effective, such a system should be:

- o small, lightweight and completely self-contained
- o simple enough for inexperienced personnel to operate
- o capable of operation without electricity
- o fabricated to allow access only to user oriented portions
- o independent of ambient temperature and pressure fluctuations
- o stable enough to maintain calibration within $\pm 2\%$.

DEVELOPMENT AND LABORATORY

A prototype was constructed by the National Bureau of Standards (NBS) in 1974 and delivered to EMSL-RTP for evaluation. This system which was housed in an aluminum briefcase, utilized a set of capillary tubes to deliver fixed flows of SO_2 gas standard from a cylinder into a diluent stream of SO_2 free (zero) air. EPA's initial testing of this device indicated that it was unable to generate repeatable ($\pm 2\%$) SO_2 concentrations. A decision was made to redesign the system and under contract, construct five second generation devices for further testing and evaluation.

The second generation devices (Figure 1) contained two flow paths, pollutant and diluent, converging in a mixing chamber (Figure 2). The diluent path consisted of a pressure regulator with gauge and a 5 liter/minute porous plug restrictor. The pollutant path consisted of a pressure regulator with gauge, a Teflon cross containing three porous plug restrictors, and three toggle valves. The use of toggle valves made it possible to produce seven discrete SO_2 concentration levels.

After receipt of the second generation devices, the Quality Assurance Division (QAD) of EMSL began a series of tests designed to characterize the porous plug restrictors. Of major concern was the effect of temperature and delivery pressure upon the system as a whole.

Temperatures were varied in an environmental chamber from 20 to 30 degrees centigrade (the normal operating range of most SO_2 analyzers). The system's output calibration remained constant throughout this range indicating that temperature fluctuations would not adversely affect performance.

The SO_2 delivery pressure (measured by front panel gauges) was varied from 10 to 50 psig. Flows were found to vary linearily with gauge pressure. A specification was then written covering the precision and resolution of gauges to be used in any future devices.

Since the devices would be utilized at different barometric pressures, there was concern about the repeatability of the original SO_2 output concentrations. Flow rates were measured daily for a period of ten days. This testing indicated that the individual flows (pollutant and diluent) varied with barometric pressure changes, but the seven flow ratios (pollutant/total) which determined the SO_2 output levels, remained constant. Thus reproducible SO_2 output levels were obtainable in spite of barometric pressure changes.

The five, second generation devices were then subjected to extensive stability and precision testing. Each device was tested on ten consecutive days at a constant temperature (25°C) with the diluent and pollutant gauges set at 30 psig. All seven output concentrations were generated and analyzed on two separate analyzers (FPD and pulsed fluorescence). Mean SO_2 values for one of these devices is shown in Table 1. The slopes of all analyzer responses vs. theoretical concentrations were stable ($\pm$2%) over the 10 day period.

FIELD EVALUATION

Test results so far indicated that the systems operated as expected within a laboratory environment. Studies were then undertaken to determine their usefulness as field auditing devices. A device was shipped from RTP to a laboratory on the west coast. The device was taken to a high altitude site (630 mm Hg) and, as expected, flows at this site differed considerably (5-8%) from those measured at RTP. However, since the low barometric pressure affected the operation of the pollutant and diluent flow restrictors equally, the flow ratios and, therefore, the SO_2 output concentrations were the same.

The device was returned to the laboratory and then shipped by truck to Montana for an actual field audit. When the audit was completed and the device returned to the laboratory, a large dent was noted in the aluminum case. Despite the harsh treatment and apparent damage, no glassware was broken and the SO_2 outputs continued to remain constant.

Evaluation of all test data indicated that the dilution systems were functioning properly and would serve well as SO_2 continous monitor auditing devices. Thus in 1979, QAD contracted to have 20 devices built.

ACCEPTANCE TESTING

These twenty units were received in December 1979, and acceptance testing was initiated immediately. A change in laboratory procedures revealed a construction flaw not readily apparent. Previously, QAD personnel had measured flows with bubble flowmeters; however, flows were now measured with laminar flow elements (LFE's). It was subsequently found that, depending on the flow, the LFE produced back pressure of 15 to 220 millimeters of water. This back pressure, in turn, produced sufficient leakage within the device to cause non-repeatable flow measurements.

Further investigation revealed that the tubing to glassware connections between the flow restrictors and the dilution chambers could not withstand even a small pressure. Thus another dilution chamber, which has proven successful in a QAD electronic, mass flow controlled audit device, was substituted for the original. It consisted of two small 65cm^3 chambers containing vortex shedders designed to create turbulence (see Figure 2). The inlet and outlet tubing-to-glass connections were made with teflon or nylon unions. The glass connections were lightly sandblasted to prevent slippage of the unions, and only Teflon ferrules were used in contact with glass. When three devices were equipped with these new chambers, the tests showed that the new chambers were satisfactory, so the remaining audit devices were modified.

Final acceptance testing was conducted from March 13, 1980 to May 7, 1980. At the beginning of the tests, an SO_2 analyzer was calibrated using a high concentration (96 ppm) SO_2 cylinder standard (previously certified to an NBS srm cylinder) and two NBS SRM SO_2 permeation tubes. After the initial 5-point calibration the monitor was checked with three SO_2 levels; zero, span and a midpoint, before and after testing each audit device. If any of the three points varied by more than 1.5 percent from the initial calibration curve, a new calibration was performed.

After the analyzer calibration was checked, each morning, an audit device was prepared for testing. A cylinder of SO_2 (approximately 50 ppm) was connected, and the pollutant pressure gauge was adjusted to 30 psig. The system was purged for 15 minutes with SO_2 to saturate the pollutant flow path and equilibrate the surfaces. During this pruging period, the flow for each of the toggle valves (1,2,3) was measured and recorded. The total pollutant flow of all valves open (1+2+3) was also measured and recorded. All toggle valves were closed and zero air supplied to the device from the same clean air source as used to calibrate the monitor. The diluent pressure gauge in the device was also set to 30 psig and the flow measured and recorded. Two LFE's were used to cover the pollutant flow range, and another was used for the diluent air. Two hundred and sixteen flow measurements were taken over a span of 63 days by two different people working independently. The measured total flow (valves 1+2+3) was subtracted from the summation of the measured separate flows (valves 1,2,3) and then divided by the measured total flow to give a percent difference. This was done for the set of flows for each device, then averaged. The mean of the percent differences between the measured total pollutant flow and the summation of flows was -0.48% with a standard deviation of .236%; an indication of excellent flow precision.

Using the device's three toggle valves, four upscale SO_2 levels and a zero were generated. Each level was analyzed by the SO_2 monitor until a stable trace of the monitor's output was observed on the strip chart recorder. The span point (valves 1+2+3) was generally run first, and then SO_2 levels were generated in descending order of concentration (valve 1, valve 2, valve 3). Each device was tested once each day on three different days. At the end of each test the analyzer calibration was checked again using an SO_2 cylinder for the span point, a permeation tube for the mid-point, and the same clean air supply for a zero. The diluent air flow remained at a fixed value for the span, mid-point and zero checks.

These four upscale SO_2 concentration levels presented equally impressive accuracy data. A measured output level was compared with the corresponding calculated output level (see Table 2). The calculated output (CO) was obtained by multiplying the cylinder concentration (CC) by the pollutant flow (PF) for that specific toggle valve and dividing by the sum of the diluent (DF) and pollutant flows (PF).

$$CO = \frac{(CC) \times (PF)}{(DF + PF)} \qquad (1)$$

The measured output (MO) was subtracted from the calculated output (CO) and divided by the calculated output to obtain a percentage difference at each level.

$$\% \text{ Difference} = \frac{CO - MO}{CO} \times 100 \qquad (2)$$

The percentages at each level were then averaged for all devices. Percentage differences were used because the output levels were not identical for all devices. For the level generated using valves 1+2+3, the mean of the percent differences for all devices was -1.72% with a standard deviation of 1.56%; for valve 1, the mean of the percent differences was -1.78 with a standard deviation of 1.55; for valve 2, the mean of the percent differences was 0.23% with a standard deviation of 3.09%; the mean of the percent differences was +1.33% with a standard deviation of 5.99%. These numbers were obtained by two people over a 2 month period. While the devices seem to exhibit a slight SO_2 loss at the lower concentrations, the percent differences fell within the expected QAD acceptance criteria.

These acceptance test results and the laboratory and field evaluation of the second generation prototypes provided QAD with realistic values for the device's precision and accuracy. Performance specifications were established based on these data, and pre- and post audit procedures were written.

PRE-AUDIT TEST PROCEDURES

Each device must meet the following pre-audit requirements before being used for an audit;

(1) each device must be verified (its output concentrations remeasured) on two different days in the laboratory to establish repeatability,

(2) the percent difference between each valve combination's calculated concentration and its measured concentration must be less than two percent (except for the lowest concentration (valve No. 3), which must be less than five percent),

(3) the zero air cylinders must be analyzed to assure that they are too contaminated with SO_2, and

(4) the audit cylinders must be verified against an NBS/SRM.

To determine the calculated and measured output concentrations (Specification No. 2) a specific procedure is followed: 1) Flow measurements are taken on the audit device using LFE's and a micro-manomters, 2) Flows for all possible valve combinations plus the dilution flow are measured, 3) These measurements are conducted for each device on three different days, 4) Average flows are calculated from the three days of data, 5) A dilution ratio is calculated for each possible valve combination from these averages, using the following formula:

$$\text{Dilution Ratio} = \frac{\text{Pollutant Flow}}{(\text{Pollutant Flow} + \text{Dilution Flow})} \qquad (3)$$

After the dilution ratios for each device are determined, they are verified with a calibrated laboratory SO_2 analyzer. The laboratory analyzer is calibrated initially using an NBS SRM permeation tube. The analyzer is then zeroed and spanned daily, using an NBS SRM cylinder of SO_2. The devices are then set up according to field instructions, except that house zero air is used instead of zero air cylinders. Regulators are attached to the SO_2 cylinders, evacuated and pressurized a minimum of three times, and then left pressurized for not less than twenty-four hours before being used. After the equilibration period, the SO_2 delivery pressure is adjusted to 50 psig. Zero air is connected to the "air input" bulkhead fitting. The exhaust is connected to a suitable exhaust hood, and initially the bulkhead fitting labeled "pollutant sample output" is capped. The pollutant pressure gauge is adjusted to approximately 50 psig, the toggle valves are opened, and the system is purged for twenty minutes. After the purge is completed, the pollutant pressure gauge on the audit device is adjusted down to 30 psig. These pressures are monitored and readjusted, as needed, for about five minutes until the pressure regulators "settle in." As soon as they stabilize, the "pollutant sample output" is uncapped and connected to the sample input of the calibrated SO_2 analyzer. The first SO_2 level (valves 1+2+3, open) is allowed to stabilize and a reading taken. The remaining valve combinations are run in descending concentration order to minimize equilibration times, and the calculated concentration for each valve combination is derived by the formula (1) The percent difference between the measured output concentrations and the calculated output concentrations is derived using the formula (2) This pre-audit calibration procedure is duplicated on a following day to assure device repeatability. The zero air and audit cylinder concentrations are verified on two different days as well. Verification is performed utilizing an analyzer calibrated with an NBS/SRM. Once these pre-audit procedures are complete, the device, with the appropriate instructions, is ready to be shipped to the audit site. Step-by-step user instructions are sent with a data card to each audit participant. All agencies associated with the State and Local Air Monitoring Stations (SLAMS) network are required to participate in the ambient SO_2 audit program. Due to the limited number available, devices are mailed out on a rotating basis.

POST-AUDIT PROCEDURES

When returned to the lab, the devices undergo post-audit testing to assure that the flow ratios and output concentrations are still within the prescribed specifications. If they are outside the limits, corrective steps are taken (i.e., change faulty parts, fix leaks, remeasure flows and/or reanalyze the cylinder concentration).

Whe the audit adta is returned to QAD, a linear regression of the audited analyzer's concentration (Y) versus the true or audit concentration (X) is calculated (Figure 3). A copy of this regression data is then sent to the participant. The results of each year's audits are stored on magnetic disks. If the audit device is shown to be defective by the post-audit tests and the data cannot be corrected, then another audit is scheduled.

AUDIT RESULTS

From the first field audit in October 1980 through December 1982, these devices have been used to audit 303 SO_2 analyzers. Their overall rugged design has proven itself well. To date, only four glass mixing chambers have been broken, three pressure gauges replaced, two internal regulators have failed, and only one set of flow restrictors has been plugged. QAD specifications for the audit device have been exceeded only 40 times or thirteen percent of the audits. Eighty percent of these occurrences have been flow changes of less than or equal to 4%. Figure 4 shows the distribution of the flow changes for valve No. 1 as determined by the post audit tests. Flows generally decrease with time as the pressure gauges become less sensitive or are altered due to transportation shock.

Table 3 is a compilation of the audit data from October 1980 through December 1981; Table 4 shows the data from January through December 1982. The 1980/81 data shows a mean slope of 0.95 whereas the 1982 data shows a mean slope of 0.98, indicating an increase in SO_2 data quality.

QAD audit ratings are as follows: if the slope is between 0.95 and 1.05, an "Excellent" rating is assigned; if the slope is between 0.85 and 0.95 or between 1.06 and 1.15, a "Satisfactory" rating is assigned. If it is not within ±15 percent of the calculated value then it is an "Unsatisfactory" audit. In the 303 audits the following percentages were in each category:

1980/81		1982
43%	Excellent	62%
42%	Satisfactory	33%
15%	Unsatisfactory	5%

CONCLUSIONS

Results from developmental testing, evaluations, final acceptance tests and finally, actual audits have shown that extensive testing and refinements have produced a very reliable and accurate SO_2 ambient auditing device. QAD now has a system by which it can monitor the quality of ambient SO_2 data.

QAD has ordered twenty more audit devices and is presently introducing these into the National Performance Audit Program. A similar device to audit NO_2 and O_3 is presently undergoing final acceptance tests. This audit program is scheduled to begin in the fall of 1983.

ACKNOWLEDGEMENTS

We would like to thank the Research Triangle Institute who constructed the second generation prototypes, did the temperature and pressure testing, and provided QAD with numerous evaluations; Rockwell International, Environmental Monitoring and Services Center for evaluating the second generation prototype, procedures, and the final product; and especially Northrop Services, Inc., not only for evaluations and testing, but also operating the ambient SO_2 audit program.

Table 1. Prototype #4 precision and stability data.

	Valve # Open						
Run #	1,2,3	2,3	1,3	3	1,2	2	1
1	0.900	0.840	0.695	0.622	0.289	0.216	0.070
2	0.904	0.834	0.689	0.620	0.286	0.216	0.070
3	0.912	0.840	0.698	0.626	0.288	0.217	0.073
4	0.907	0.842	0.699	0.627	0.289	0.219	0.070
5	0.906	0.840	0.698	0.625	0.289	0.219	0.072
6	0.904	0.840	0.694	0.630	0.291	0.221	0.070
7	0.906	0.840	0.695	0.627	0.289	0.216	0.069
8	0.908	0.839	0.700	0.626	0.288	0.220	0.070
9	0.910	0.844	0.700	0.624	0.290	0.217	0.072
10	0.898	0.832	0.696	0.621	0.287	0.217	0.071
Average	0.906	0.839	0.696	0.625	0.289	0.218	0.071
Std Dev	0.004	0.004	0.003	0.003	0.001	0.002	0.001

Table 2. Acceptance testing data device no. E102.

Day	Open Valve No.	STP Flow cc/min	Device Output ppb SO_2 Measured	Calculated
1	1,2,3	67.782	605	602
	1	43.492	390	388
	2	18.651	166	167
	3	6.084	54	55
	Dilution Flow	5143.6		
2	1,2,3	66.455	611	596
	1	42.475	390	383
	2	18.253	165	165
	3	5.967	53	54
	Dilution Flow	5096.9		
3	1,2,3	66.095	606	597
	1	42.391	391	384
	2	18.214	166	166
	3	5.940	53	54
	Dilution Flow	5063.0		

TABLE

1980/81 AUDIT RESULTS
SO2 DILUTION SYSTEM

VALVES	APPROX. CONC.	N	MEAN DIFF. ppm	MEAN DIFF. %	STD. DEV. ppm	STD. DEV. %
1+2+3	.700	21	−.061	−8.6	.120	17.0
1	.450	139	−.023	−4.9	.053	11.6
2+3	.250	150	−.011	−4.4	.029	11.8
2	.190	150	−.009	−4.4	.023	12.0
3	.060	148	−.003	−4.0	.010	16.5
ZERO		150	+.001		.003	

	N	MEAN	STANDARD DEVIATION
SLOPES	150	.9509	.1168
INTERCEPTS	150	.0009	.0046

TABLE 4.

1982 AUDIT RESULTS
SO2 DILUTION SYSTEM

VALVES	APPROX. CONC.	N	MEAN DIFF. ppm	MEAN DIFF. %	STD. DEV. ppm	STD. DEV. %
1+2+3	.700	22	−.010	−1.6	.057	8.1
1	.450	151	−.009	−2.0	.048	10.2
2+3	.250	153	−.004	−1.5	.027	10.2
2	.190	150	−.003	−1.5	.020	10.0
3	.060	152	−.001	−1.7	.007	11.2
ZERO		153	+.001		.003	

	N	MEAN	STANDARD DEVIATION
SLOPES	153	.9805	.1025
INTERCEPTS	153	.0007	.0036

FIGURE 1. DILUTION SYSTEM

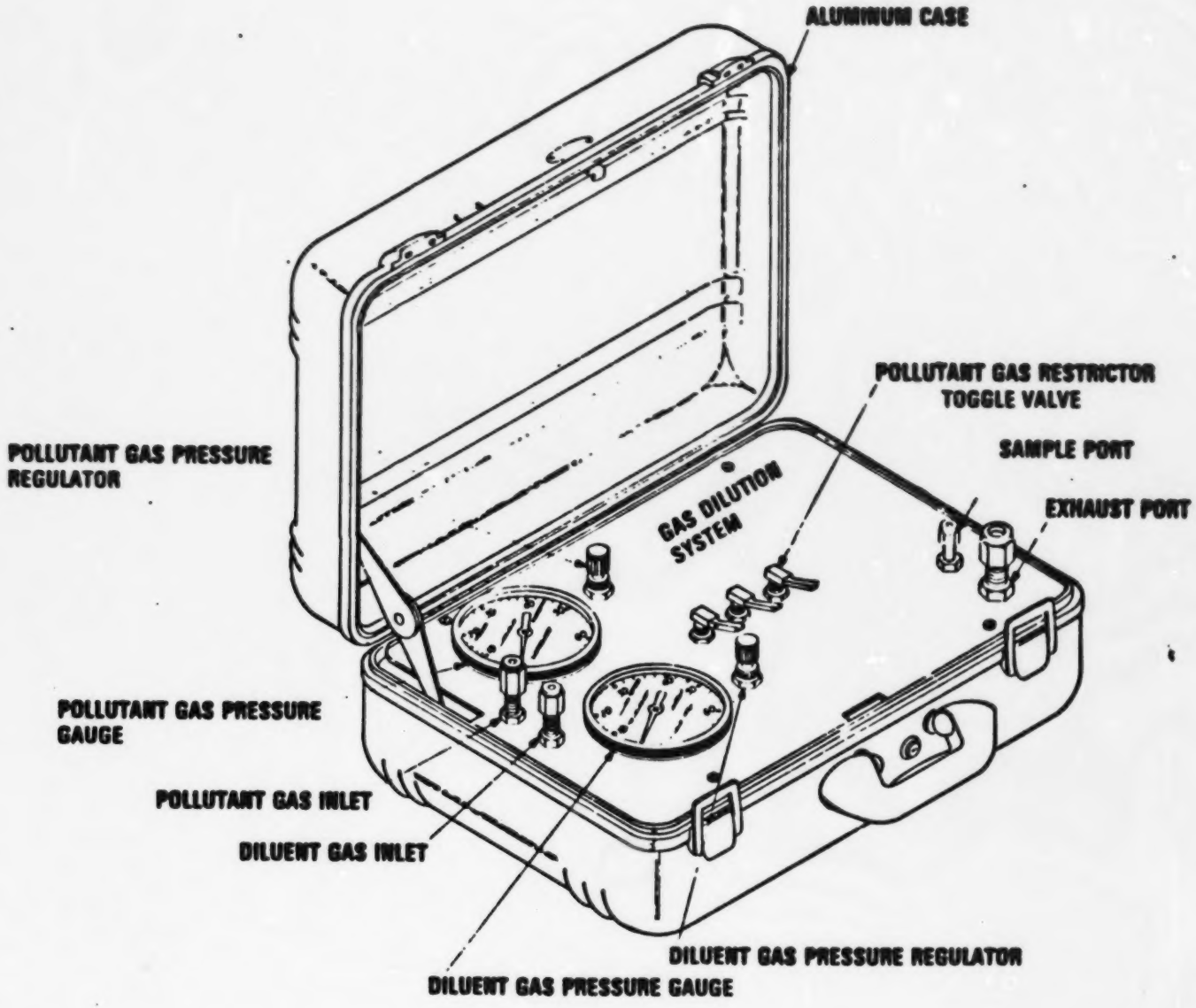

FIGURE 2.

DILUTION SYSTEM SCHEMATIC

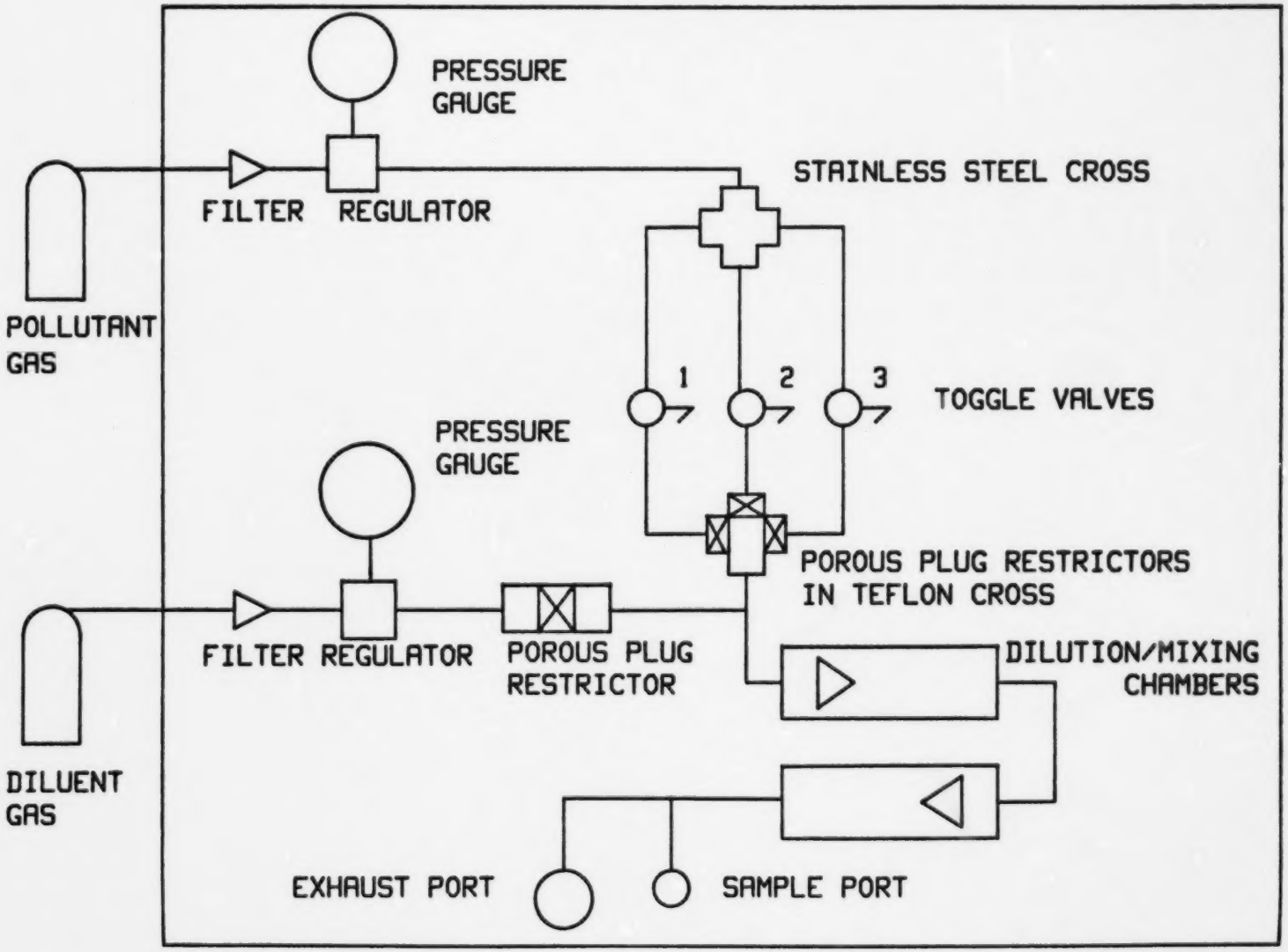

FIGURE 3

INTERLABORATORY AUDIT RESULTS

SO2 DILUTION SYSTEM

1982

LAB No. 314001
NAME:
AGENCY:
ADDRESS:

DEVICE No. 112
SAROAD No. 500280004E01
SITE No. 1
METHOD: 31 Fluorescence
Date code: 02.055
REC. #: 1

VALVES	INDICATED	ACTUAL	DIFFERENCE	% DIFFERENCE
1	.408	.404	-.004	-1.0
2+3	.218	.219	-.001	-.5
2	.165	.167	-.002	-1.2
3	.052	.053	-.001	-1.3
ZERO	.001	0.000	.001	

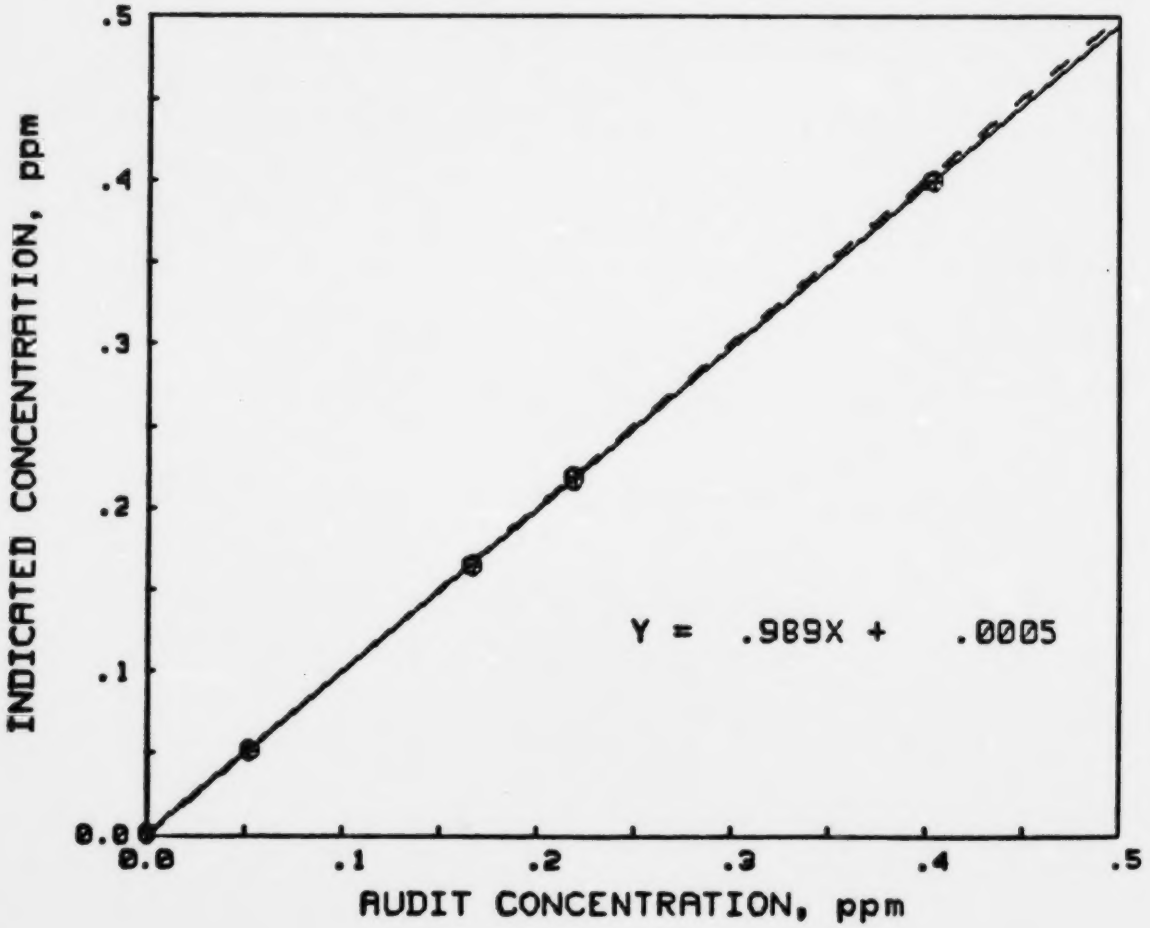

FIGURE 4

SO2 AUDIT DEVICES
% FLOW CHANGE FOR VALVE #1

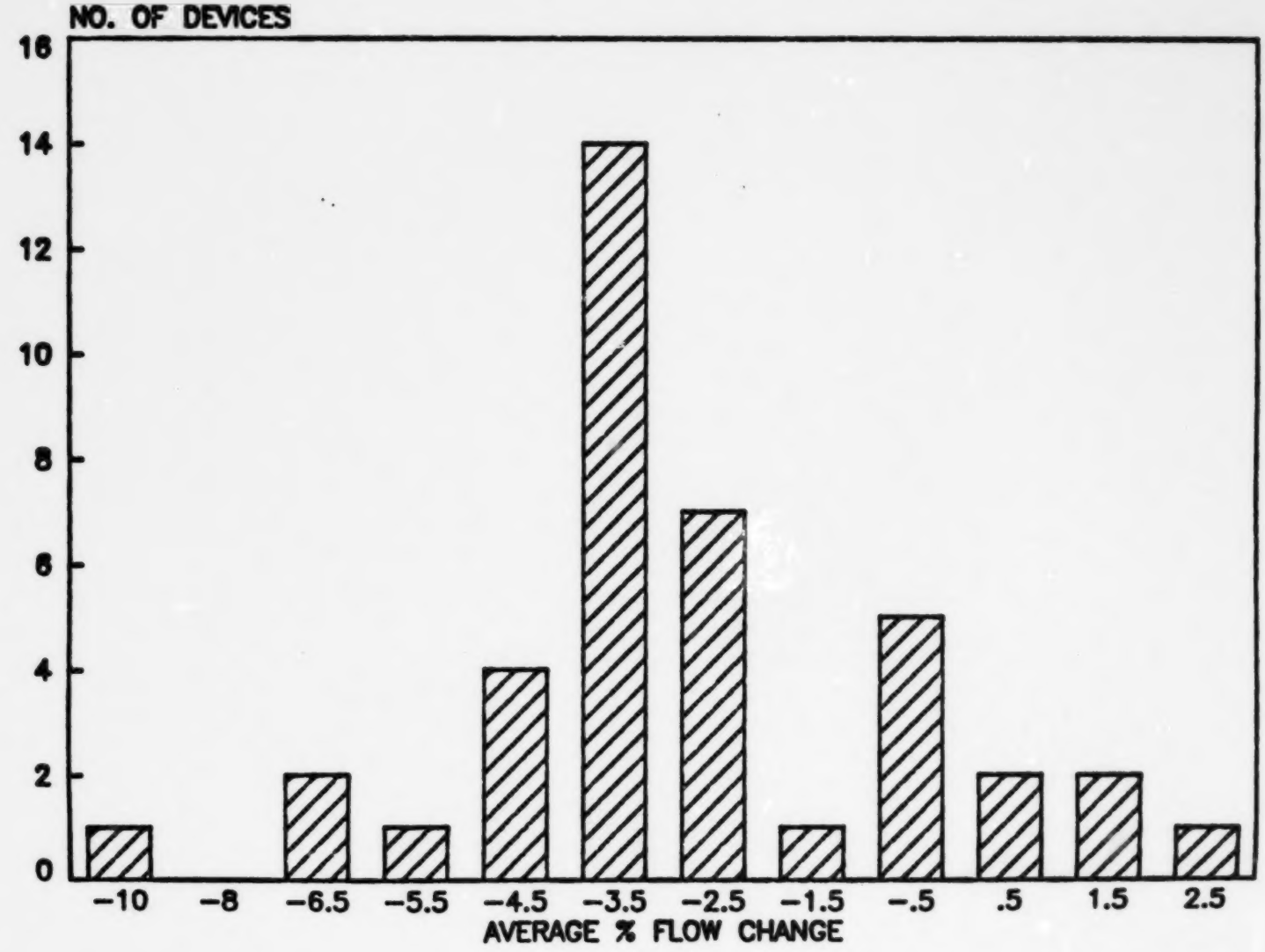

FIGURE 3

INTERLABORATORY AUDIT RESULTS

SO2 DILUTION SYSTEM

1982

LAB No. 314001
NAME:
AGENCY:
ADDRESS:

DEVICE No. 112
SAROAD No. 500200004E01
SITE No. 1
METHOD: 31 Fluorescence
Date code: 82.055
REC. #: 1

VALVES	INDICATED	ACTUAL	DIFFERENCE	% DIFFERENCE
1	.488	.484	-.004	-1.0
2+3	.218	.219	-.001	-.5
2	.165	.167	-.002	-1.2
3	.052	.053	-.001	-1.3
ZERO	.001	0.000	.001	

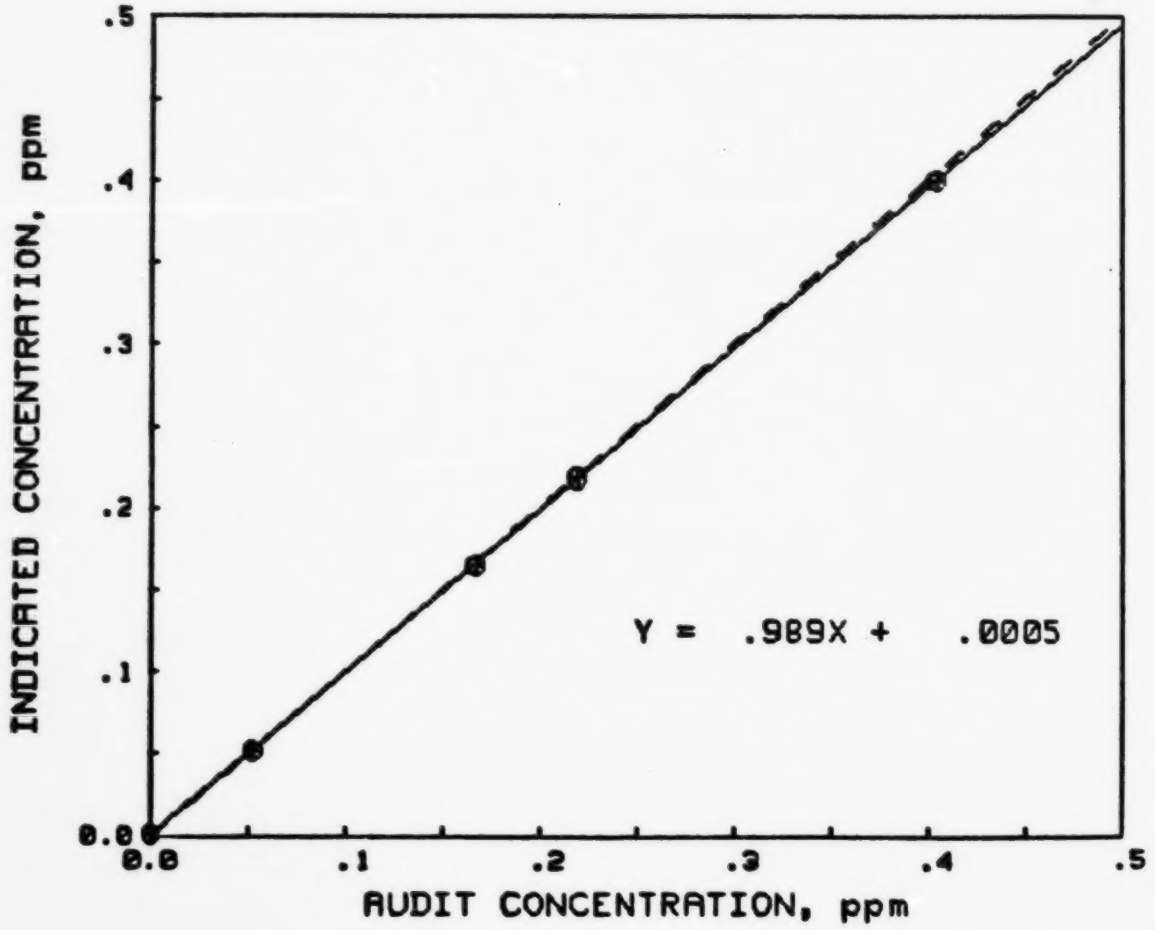

FIGURE 4

SO2 AUDIT DEVICES
% FLOW CHANGE FOR VALVE #1